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Lead and other heavy metals in soils impacted by exterior legacy paint in residential areas of south west England

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Abstract

Legacy paint on publicly-accessible structures in residential areas of Plymouth, UK (a bridge parapet, hospital railings, a goal frame, urban street paving and a telephone kiosk) and local paint-contaminated soils have been analysed for lead and other heavy metals (chromium, zinc and barium) by x-ray fluorescence spectrometry. Lead was detected in all paints analysed (n = 56) apart from two fragments of yellow road markings, with maximum concentrations exceeding 300 g kg^{-1}. Soils were contaminated by Pb to varying degrees that depended on the condition and Pb content of the paint applications and the nature and vegetation of the soil, with a maximum concentration of 27 g kg^{-1} and a maximum enrichment factor normalised to grain size and regional baseline soil of 270. While Cr showed no clear contamination in soils that could be attributed to paint, contamination from this source was evident for Zn in soil by the goal frame and for Ba and Zn in soil by the bridge parapet. Application of a physiologically-based extraction test to the soils revealed stomach bioaccessibilities that were variable among the samples and between the metals but that were greatest for Zn and lowest for Cr. With the exception of Cr, bioaccessibility generally decreased in the intestine, with mean intestinal bioaccessibilities relative to total metal of about 6% for Pb and Ba, 0.9% for Cr and 1.6% for Zn. From both a health and environmental perspective, Pb is the heavy metal of greatest concern because of its common occurrence at high concentrations in extant paints, coupled with a relatively high bioaccessibility and well-documented chronic neurotoxicity. Public exposure to Pb in residential areas may arise through direct contact with paint or soil or via the intrusion of contaminated geosolids to the household on shoes or as airborne dust.

Keywords: leaded paint; heavy metals; residential; exterior; soils; bioaccessibility

1. Introduction

Because of the well-documented acute and chronic toxicities of Pb, and in particular its neuro-toxicological impacts on young children, contemporary and legacy sources of the metal have come under intense scientific scrutiny and increasingly strict regulation over the past few decades (Wadanambi et al., 2008; Holecy and Mousavi, 2012; Datko-Williams et al., 2014). Despite restrictions on or the phasing out of Pb in most applications, the widespread occurrence of elevated concentrations in soil remains a concern from both an environmental standpoint and a health perspective (Luo et al., 2012; Walraven et al., 2015). In urban and residential settings with no distinctive industrial sources (e.g. from mining, smelting or waste processing or disposal), the principal routes of Pb accumulation in soil are believed to be via the historical combustion of leaded gasoline and the historical use but contemporary removal or weathering of exterior Pb-based paints (Clark et al., 2006; Laidlaw and Filippelli, 2008). More specifically, while leaded gasoline is likely to be the dominant source of Pb in soil in the centres of large cities (Mielke et al., 2008), exterior paint may be the larger source in smaller urban and suburban communities (Clark and Knudsen, 2013). Given that an appreciable percentage of Pb inside the household is derived from outdoor dusts and soils (Laidlaw et al., 2014), exterior paint may also, in many cases, represent a significant, if not the principal source of indoor Pb.

In a recent study conducted within Plymouth, a small (~ 250,000 inhabitants) coastal city in south west England, leaded paint was found to be abundant on a range of publicly-accessible painted structures and street furniture, including bollards, telephone kiosks, pillar boxes, bridge parapets, railings, guttering and playground equipment (Turner and Solman, 2016). Since such structures are common throughout

the UK, flaking legacy paint from poorly maintained structures was considered a significant, general source of environmental Pb in the urban and suburban settings and, as such, an important indirect source of Pb to the contemporary residential household.

The present study builds on these observations by re-visiting selected structures where layering and flaking of leaded paint was evident in order to evaluate the impact of external paint on the contamination of local soils by Pb and other heavy metals. Specifically, the contamination of Pb, Cr, Zn and Ba is estimated from measurements of metals in flaking paints and in local and baseline soils, and the bioaccessibility of these metals in paint-impacted soils is determined using a two-stage physiologically-based extraction test (PBET) that simulates, sequentially, the chemical makeup of the human stomach and intestine.

2. Materials and methods

2.1. Sampling, sample preparation and sample characterisation

Sampling targeted structures accessible to or used by the public and that were located in residential areas within 5 km of the centre of Plymouth or in a small community located on Dartmoor National Park and about 15 km to the north of the city. In Plymouth, paint was sampled in dry weather during October 2016 from one of two panelled 20 m x 1.5 m steel parapets of a road bridge (with no road markings) over a disused railway, the 2-m high wrought iron railings demarking the 500-m perimeter of a hospital, yellow parking lines applied to the paved edge of a residential city street, and one of two ~ 4 m x 1 m steel goal frames in a children's play park. On Dartmoor, paint was sampled in November 2016 from a rectangular, 2.5 m x 1 m cast iron-

timbered door K6 telephone kiosk in the village of Dousland (50.5006; -4.0670). All structures were within 20 m of private residences with the exception of the goal frames which were within 15 m of the boundary of a primary school. Up to 10 paint flakes of between ~ 2 and 20 mm in length were retrieved with plastic tweezers from accumulations at the foot of each structure or from painted surfaces where extensive flaking was visible and were stored in specimen bags and in the dark pending analysis.

Triplicate samples of about 30 g of surficial soil were collected using a plastic spatula on the same occasions as the corresponding paint samples were retrieved and at locations in the immediate vicinity of each structure that were most likely to receive the greatest pedestrian disturbance. Specifically, samples were taken from soils adjacent to the pavement and within 1.5 m of the bridge parapet, railings and road paint, road verge soil about 0.5 m from the access door of the telephone kiosk, and soil at a distance of 0.5 m from the goal frame mouth and where the turf had been most trampled. Where possible, and in order to examine spatial variation in metal contamination, additional soil samples were collected at different distances (up to 5 m) from the structures and along an axis that was normal to the main face. Regional baseline soils were collected from an area of a small urban park that was within 10 m of an unpainted section of road (urban roadside baseline), the playing fields adjacent to the children's play park (park baseline) and a roadside verge on Dartmoor that was remote from any residential areas (National Park baseline). After being transported to the laboratory in individual specimen bags, samples were oven-dried in crucibles at 105 °C for 24 h before stones, fragments of glass, leaves and other debris were removed. Samples were then sieved through 2 mm and homogenised in a series of

agate bowls, each containing five agate milling balls, using a Fritsch planetary mill (model Pulverisette 5) at 300 rpm for 3 min. In a fume cupboard, milled samples were packed into individual polyethylene XRF sample cups (Chemplex series 1400, 21-mm internal diameter) that were collar-sealed with 3.6 μm SpectraCertified Mylar polyester film.

The pH of at least one soil sample from each site was measured using a Meterlab PHM210 pH meter and Hach pHC2051-8 electrode after 5 g portions of dried material had been equilibrated with 12.5 ml aliquots of deionised water in a series of 50 ml polypropylene centrifuge tubes. Loss on ignition (LOI) was determined on soil samples as a measure of organic content by determining the weight loss of ~ 3 g aliquots of dried material after combustion at 550 ºC for 5 h in a Carbolite AAF1100 furnace.

2.2. XRF analysis

Paint fragments and homogenised soil samples were analysed in the laboratory using a Niton XL3t 950 He GOLDD+ portable XRF housed in a 4000 cm^3 accessory stand. The heavy metals Pb, Cr, Zn and Ba were the focus of the present study because of their extensive historical use in exterior paints, but Fe, Mn, Ca and Rb were also recorded in soils as elements of geochemical significance. Depending on condition and degree of contamination from the underlying (e.g. rusting) substrate, one or both sides of paint samples were analysed in a low density, plastics mode with thickness correction after sample thickness had been measured using digital callipers. Fragments were suspended above the 10 mm detector window on Mylar film before measurements of 60 s, comprising successive counting periods of 30 s each at 50

kV/40 μA (main filter) and 20 kV/100 μA (low filter), both with 3-mm collimation, were activated remotely through a laptop. Spectra were quantified by fundamental parameter coefficients to yield elemental concentrations on a dry weight basis (in μg g^{-1}) and with a measurement counting error of 2σ (95% confidence) that were downloaded to the laptop via Niton data transfer (NDT) software. Regular analysis of two Niton polyethylene discs certified for Pb, Cr and Ba (PE-071-N and PN 180-619) returned concentrations of that were within 5% (Pb and Cr) or 15% (Ba) of reference values, and measurement limits of detection (LOD), defined herein as 3σ for samples of the lowest fluorescence intensities, were about 20, 7, 60 and 400 mg kg^{-1} for Pb, Cr, Zn and Ba, respectively.

Soil samples contained within polyethylene XRF cups were analysed in a higher density mining mode. Here, cups were placed centrally over the detector window with the collar-sealed Mylar surface face-down, and measurements were conducted for 90 s, and without collimation, comprising successive counting periods of 30 s each at 50 kV/40 μA (main filter), 20 kV/100 μA (low filter) and 50 kV/40 μA (high filter). Concentrations were downloaded to the laptop as above, with corresponding measurement LODs of about 5 mg kg^{-1} for Pb and Rb, mg kg^{-1} for Cr, Zn, Fe and Mn, and 50 mg kg^{-1} for Ba and Ca. Regular analysis of Sigma-Aldrich RTC loams certified for Pb, Cr and Zn and packed in XRF cups (MSL-100, MSM-100, MSH-100, MSL101, MSM-101 and MSH-101) returned concentrations that were within 10% of reference values.

2.3. Physiologically-based extraction test

175 Soil samples were subject to an in-vitro physiologically based extraction test (PBET)
176 that mimics, sequentially, the chemical conditions in the human stomach and
177 intestine. The method is described in detail by Ruby et al. (1996) and Karadaş and
178 Kara (2011) and was undertaken herein using analytical-grade reagents study
179 purchased from Fluka, Sigma-Aldrich or Fisher. Briefly, the gastric solution was
180 prepared by dissolving 1.25 g porcine pepsin, 0.50 g sodium citrate, 0.50 g sodium
181 malate, 420 μL of lactic acid and 500 μL of acetic acid in to 1 L of Milli-Q water and
182 adjusting the contents to pH 2.5 with concentrated HCl. About 0.5 g of each sample
183 and a solid-free control was combined with 50 mL of gastric solution in a series of
184 screw-capped polypropylene centrifuge tubes that were submerged to just below the
185 lid line in a shaking water bath maintained at 37 °C. After 1 h, 5 mL of each extract
186 was filtered through a 0.45 μm Whatman cellulose acetate filter and acidified with 0.1
187 mL of concentrated HNO_3 before being stored under refrigeration pending analysis
188 ("stomach phase" samples). Meanwhile, and following the compensatory addition of
189 5 mL of gastric solution, the pH of each extract was adjusted to 7 using a saturated
190 $NaHCO_3$ solution and 87.5 mg of bile salts and 25 mg of porcine pancreatin added.
191 The contents were then returned to the water bath and incubated for a further 4 h
192 before 5 mL aliquots were abstracted, filtered and acidified as above. In addition, and
193 before storage under refrigeration (and as "intestine phase" samples), extracts were
194 centrifuged at 3000 rpm for 5 min to remove any protein formed after the introduction
195 of the acid spike to the neutral solutions
196
197 *2.4. PBET analysis*
198 Stomach and intestinal phase extracts arising from the PBETs were analysed for Pb
199 and Zn by inductively coupled plasma-optical emission spectrometry (ICP-OES)

using a Thermoscientific iCAP 7400, and for Cr and Ba by collision cell-inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-series II (Thermo Elemental, Winsford UK) with a concentric glass nebuliser and conical spray chamber. Instruments were calibrated using four standards and a blank prepared by serial dilution of CPI International standards in 2% HNO_3, with settings described elsewhere (Turner et al., 2016; Turner et al., 2017) and LODs derived from three standard deviations arising from multiple measurements of the lowest standard of about 10 μg L^{-1} for Pb and Zn and 1 and 5 μg L^{-1} for Cr and Ba, respectively.

3. Results and Discussion

3.1. Paint fragment characteristics and heavy metal content

The structures targeted in the present study are illustrated in Figure 1, while results arising from the analysis of paint fragments (n = 56) sampled from each structure are shown in Table 1. Overall, and among the metals studied, Pb was the most pervasive, being detected in all but two cases and at concentrations that always exceeded the US urban abatement action level of 5000 mg kg^{-1} (Turner and Solman, 2016). While Ba was detected in some or all fragments from each structure, Cr and Zn were never detected in paint fragments from the goal frame and street paints, respectively. Other elements that were detected less frequently but not considered further included Bi, Cu, Ni, Sn, Sb and V and, while Fe was present in many samples, its presence was generally attributed to contamination from the underlying metallic or paved substrate.

Figure 1: The painted structures considered in the present study. (a) The steel parapet of a road bridge over a disused railway, (b) the paved edge of a city street, (c) railings around Plymouth Eye Hospital, (d) the vertical post of a goal frame in a play park, and (e) a telephone kiosk serving a small community on Dartmoor.

The parapets of the road bridge had been overpainted several times and in different colours (but mainly white, grey, blue and lilac) and the surface was heterogeneous and highly crazed. Fragments retrieved were usually multi-layered, with a thickness that ranged from about 0.8 to 1.6 mm, and concentrations of Pb were highly variable, with a maximum content of 300,000 mg kg^{-1} returned for the outer white surface of paint taken directly from the base of the right-hand panel shown in Figure 1a. While the

detection of Cr was limited to five paint fragments from the parapet and to concentrations less than 500 mg kg^{-1}, Ba and Zn were present in all fragments analysed, with the highest concentrations (above 10,000 mg kg^{-1} and 100,000 mg kg^{-1}, respectively) encountered in bluish-grey and white formulations. These observations are consistent with the occurrence of multiple, historical applications of paint of differing Pb content that include leaded zinc oxide (a mixture of basic lead sulphate and zinc oxide) but not brightly coloured lead chromates, and the pervasive use of Ba (e.g. $BaSO_4$) as a filling agent.

The hospital railings were rusting throughout, with residual black paint of limited thickness (< 0.1 mm) and layering but that was readily flaking. All paint fragments retrieved contained less variable concentrations of Pb than those on the railway bridge, with an average content of 100,000 mg kg^{-1}, and Cr, Zn and Ba were detected in a limited number of cases and at concentrations below 250 , 5000 and 1000 mg kg^{-1}, respectively. These observations suggest the historical use of a limited number of broadly similar formulations that were not based on chromates or leaded zinc oxide but that were likely comprised of white lead ($2PbCO_3 \cdot Pb(OH)_2$) that had undergone darkening and conversion to lead sulphide by the long-term contact with SO_2 in urban air.

The play park goal frame had multiple layers of white or cream paint that had been eroded to the substrate in parts, with the distribution of paint-free areas on the cross bar consistent with the gradual, long-term abrasion caused by children swinging on the structure. Lead concentrations in the paint fragments were variable and, while Cr was never detected, Zn was always present at concentrations up to 100,000 mg kg^{-1},

suggesting that leaded zinc oxide was the principal Pb-based pigment present. Although fragments were often layered (and around 0.1 to 0.2 mm thick), it was unclear whether the various applications contained different concentrations of Pb or leaded paints had been diluted with more recent lead-free formulations.

Most yellow markings at the roadside throughout the regions of the city inspected appeared to have been successively overpainted, especially where the paved surface was irregular, with older applications usually brighter and characterised by a distinctive orange hue. Fragments retrieved from the crumbling road markings along the residential street were typically between 1 and 3 mm thick and contained Pb concentrations of a few thousand $\mu g\ g^{-1}$ with the exception of two markedly paler samples derived from the top painted layer where the metal was not detected. While Ba was present in all fragments and at concentrations of a few thousand $mg\ kg^{-1}$, Zn was never detected and Cr was only detected whenever Pb was present. Concentrations of the latter metals were highly correlated ($r = 0.957$, $p < 0.01$; $n = 8$), with a slope defining the best-fit line forced through the origin of 4.62 and close to that defining the mass ratio of Pb:Cr (= 3.98) in the yellow pigment, lead chromate ($PbCrO_4$). These observations are consistent with the historical use of lead chromate in road marking paints but the more recent use of safer (albeit less brightly coloured) alternative pigments.

Paint fragments derived from the telephone kiosk on Dartmoor were different shades of red-orange and of variable thickness (0.05 to 1.3 mm) and layering, with Pb occurring at concentrations in excess of 40,000 $mg\ kg^{-1}$ throughout. Chromium, Ba and Zn were detected in all fragments and over a range of concentrations that

300 averaged 13,000, 22,000 and 4000 mg kg^{-1}, respectively. Lead and Cr concentrations
301 were highly correlated (r = 0.962; p < 0.01; n =10) but a best-fit line could only define
302 the data when an intercept was included ([Pb] = 1.713[Cr] + 50,400). The gradient of
303 the relationship suggests the presence of a lead chromate of different Pb:Cr
304 stoichiometry to that in the yellow road line paint above and/or the presence of an
305 additional compound of Cr. The former is likely molybdate sulphate red
306 ($Pb(Cr,S,Mo)O_4$), an assertion supported by the distinctive colour of phone boxes and
307 strong fluorescent peaks at 17.48 keV (Mo-Kα1) and 19.61 (Mo-Kβ1) in the paint
308 samples, while the ubiquity of Zn suggests the latter may be the anti-corrosion primer
309 and pigment, zinc chromate. The intercept of the Pb-Cr relationship also indicates the
310 presence of a leaded compound containing about 5% Pb but that does not contain Cr,
311 possibly the red, rust-proof primer, lead (II,IV) oxide ($2PbO \cdot PbO_2$).
312
313 Table 1: Number of analyses performed on paint fragments from each structure, along
314 with the number of cases in which Pb, Cr, Zn and Ba were detected and summary
315 statistics for their concentrations in mg kg^{-1} .

	bridge parapet (n = 17)	railings (n = 10)	goal frame (n = 9)	city street (n = 10)	telephone kiosk (n = 10)
Pb					
n	17	10	9	8	10
mean	126,000	100,000	49,800	3310	72,700
sd	87,200	97,200	57,100	938	30,300
median	124,000	73,700	32,200	3720	61,500
min	5960	24,200	1570	1600	42,700
max	302,000	362,000	180,000	4170	133,000
Cr					
n	5	3	0	8	10
mean	307	117		708	13,000
sd	204	88.5		226	17,000
median	207	74.5		807	3450
min	105	58.5		277	290
max	574	219		925	44,900
Zn					
n	17	7	9	0	10
mean	115,000	1770	38,400		4800
sd	153,000	2150	108,000		4470
median	3250	727	1550		3450
min	1490	153	440		665
max	363,000	5010	327,000		14,800
Ba					
n	17	3	6	10	10
mean	8460	4230	16,700	3160	22,300
sd	3040	3570	8410	761	5280
median	8690	3110	15,800	363	21,000
min	3940	1360	5630	1670	17,200
max	12,700	8220	29,400	4220	34,600

316

317

318 *3.2. Soil characteristics and heavy metal content and enrichment*

319 The geochemical characteristics of the soil samples are shown in Table 2. LOI ranges
320 from about 10% in the park baseline soil to 30% in soil in the vicinity of the hospital
321 railings, and pH is about 7 within the city of Plymouth and 6.5 on Dartmoor. Of the
322 geochemically-relevant metals reported, Fe exhibits clear evidence of contamination
323 by paint particles or the underlying metallic substrate and Ca exhibits the greatest
324 variation in concentration among the sites investigated.

Table 2: Geochemical characteristics of the soil samples in the vicinity of the various painted structures and at the baseline locations (n = 1 or 3; DNP = Dartmoor National Park). Note, LOI = loss on ignition in % and metal concentrations are given in mg kg^{-1}.

	bridge parapet	railings	goal frame	city street	telephone kiosk	urban baseline	park baseline	DNP baseline
LOI								
mean	11.4	28.8	23.8	14.0	27.2	18.0	10.9	22.2
sd				0.2	2.4			0.6
pH								
mean	6.87	7.04	7.32	7.25	6.48	7.04	7.32	6.46
sd				0.06	0.12			0.04
Fe								
mean	73,600	35,000	68,400	36,400	99,800	40,800	41,500	43,600
sd	657	383	487	102	1490	498	1820	259
Mn								
mean	1110	2050	1940	642	1340	2140	775	1180
sd	98.3	92.5	112.0	26.0	70.1	86.3	89.1	80.2
Ca								
mean	57,500	90,900	7160	37,300	22,600	47,900	3520	43,900
sd	1174	601	127	185	413	1018	147	1080
Rb								
mean	51.5	123	46.5	71.8	129	120	48.6	121
sd	2.1	3.0	0.64	0.60	28.8	3.2	2.2	12

The mean concentrations of Pb, Cr, Zn and Ba in the soil samples are shown in Table 3. In all cases, Pb concentrations in the vicinity of the painted structures are considerably higher than the corresponding baseline concentrations, with soils adjacent to the road bridge parapet and goal frame exceeding the urban and park baselines by factors of 100 and 20, respectively. The mean concentration in the bridge parapet soil is more than double the highest concentration of Pb measured in topsoils throughout England (Defra, 2012) and is comparable with the highest concentrations reported for Pb in US soils (Datko-Williams et al., 2014). While soil contamination by the remaining metals is not as pervasive, it is evident where mean concentrations are highest in the local paint formulations; specifically, Ba exhibits contamination in soils adjacent to the bridge parapet and telephone kiosk and Zn in soils by the parapet and goal frame.

The fractional contribution of Pb derived from paint particles to the local soil Pb burden, f_p, was estimated from mass balance as follows:

$$f_p = ([Pb]_s - [Pb]_b)/([Pb]_p - [Pb]_b) \quad (1)$$

where subscripts p, s and b refer to paint, contaminated soil and baseline soil, respectively, and concentrations are defined by mean values reported in Tables 1 and 2. Results of the calculations indicate an estimated contribution of Pb from paint ranging from < 0.5% for the soil by the hospital railings to over 20% for soils by the bridge parapets and the street lines. Note that equivalent calculations performed for Cr, Zn and Ba were not considered meaningful because concentration differences in the numerator or denominator were often small or negative (that is, concentrations in contaminated soils or paint fragments were close to concentrations in the corresponding baselines).

One problem with the mass balance approach above is that the heavy metal content of the source material is heterogeneous, largely because of the presence of multiple applications that are weathered differentially; this results in a range in paint metal concentration that usually spans more than an order of magnitude for each structure. Moreover, as an evaluation of local contamination, mass balance does not acknowledge potential metal leaching from residual, historical paint on the structure itself. To this end, a better measure of soil contamination is one that compares metal concentrations in contaminated and baseline soils after compensation for granulometry. Correction for grain size, or the propensity of soil particles to adsorb

368 metals, requires normalisation of concentrations with respect to an element whose
369 abundance reflects particle size, and that is conservative (or insensitive to changing
370 environmental conditions), has no significant local contamination sources and is
371 readily measurable. Since Rb satisfies these criteria, substituting for K in fine-grained
372 clays yet often absent in coarser natural particles, having very little influence by
373 anthropogenic activity and being routinely analysed by XRF (Rae, 1995),
374 concentrations measured in the soils and reported in Table 3 have been used to
375 calculate enrichment factors (EFs) for each heavy metal (Me):
376
377 $$EF = ([Me]_s/[Rb]_s)([Me]_b/[Rb]_b)^{-1} \quad (2)$$
378
379 Values of EF, shown in Table 4, can be partly understood in terms of the metal
380 concentrations in the source material and the condition of the applications. For
381 instance, high enrichment of Pb, Zn and Ba is encountered in the soil contaminated by
382 bridge parapet paint containing relatively high concentrations of these metals and that
383 was flaking extensively; conversely, enrichment below 0.5 occurs for Cr in goal frame
384 soil where the metal was never detected in paints derived from the corresponding
385 structure. In other cases, however, additional, confounding factors also appear to be
386 significant. For example, despite railing paint having a mean Pb concentration of
387 100,000 mg kg^{-1}, local soil enrichment was the lowest among the samples considered,
388 an effect we attribute to the dense coverage of unkempt vegetation around the hospital
389 that acts as protection from and aids dispersion of flaking paint particles.
390

391 Table 3: Concentrations of Pb, Cr, Zn and Ba (in mg kg^{-1} ; n = 3) in the soil samples
392 in the vicinity of the various painted structures and at the baseline locations (DNP =
393 Dartmoor National Park).

	bridge parapet	railings	goal frame	city street	telephone kiosk	urban baseline	park baseline	DNP baseline
Pb								
mean	27,200	562	1110	1050	879	236	48.3	37
sd	668	47	11	12.3	39	6	2.5	4.0
Cr								
mean	156	94.3	142	113	200	109	115	136
sd	19.3	12.8	17.3	7.1	14	11.6	7.5	13.7
Zn								
mean	4610	852	4070	710	323	322	78.8	156
sd	85	138	18.2	10.6	18	20.9	5.7	6.8
Ba								
mean	1580	320	304	629	671	305	227	127
sd	50	34	21	4.1	171	20	33	91

394

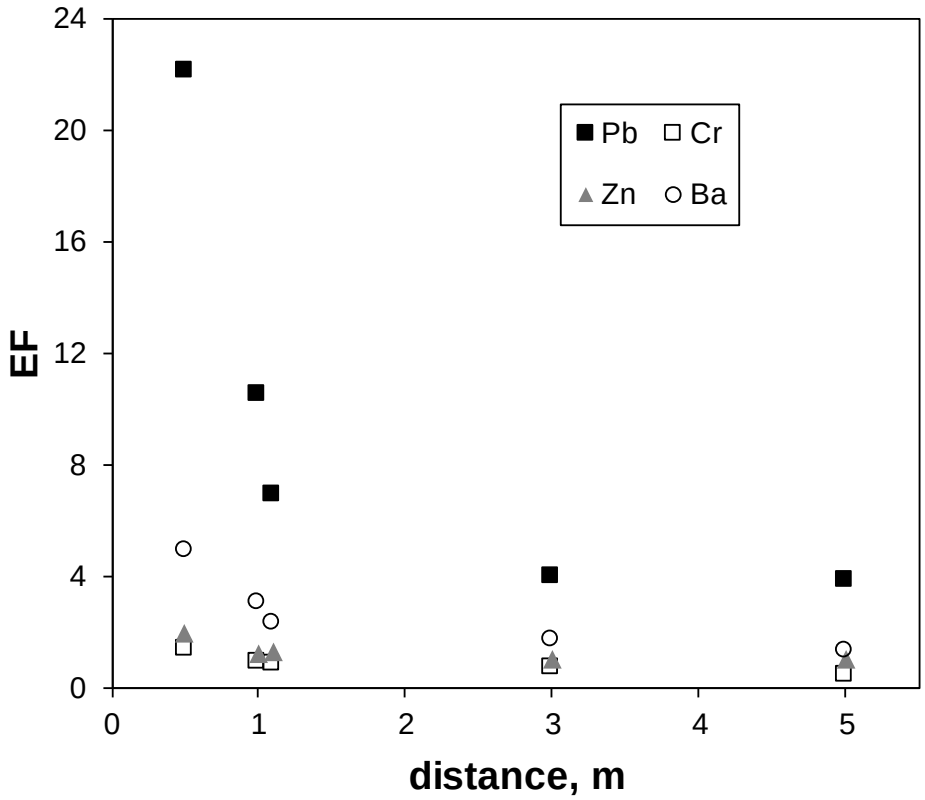
395

396 Table 4: Rubidium-normalised enrichment factors for the heavy metals in the
397 contaminated soils, calculated according to equation 2 and using the baselines
398 indicated.

	bridge parapet/ urban baseline	railings/ urban baseline	goal frame/ park baseline	city street/ urban baseline	telephone kiosk/ DNP baseline
Pb	269	2.32	24.0	7.44	22.2
Cr	3.33	0.84	0.49	1.73	1.38
Zn	33.4	2.58	54.0	3.69	1.94
Ba	12.1	1.02	1.40	3.45	4.96

399

400



401

402 *Figure 2: Heavy metal enrichment factors in soils sampled at different distances from*

403 *the door of the telephone kiosk.*

404

405 EFs were also applied to examine the spatial dispersion of paint-derived Pb, Cr, Zn

406 and Ba in soils in the vicinity of poorly-maintained structures. Results are exemplified

407 in Figure 2 for soils collected at different distances from the telephone kiosk on

408 Dartmoor, where all heavy metals were present in the paint at relatively high

409 concentrations but additional anthropogenic sources are absent. Here, values of EF

410 reveal an exponential reduction for all metals to a distance of 3 to 5 m, a distribution

411 that is characteristic of a point-source of particulate metal, like paint, rather than a

412 diffuse one (Clark and Knudsen, 2013; Thompson et al., 2014).

413

414 *3.3. Comparison of Pb and Cr concentrations in soils with SGVs*

Regarding human health and environmental protection, various countries and organisations have devised < 2 mm but non-normalised soil standards for heavy metal concentrations (CCME, 1999; Walraven et al., 2015; Vodyanitskii, 2016). In the UK, generic soil guideline values (SGVs) for both Pb and Cr were derived by the Environment Agency (2002) using the Contaminated Land Exposure Assessment (CLEA) model for three land uses. Specifically, values for Pb were 450 mg kg^{-1} for allotments and residential soils, both with and without plant uptake, and 750 mg kg^{-1} for commercial-industrial soils; for Cr, values were 130 mg kg^{-1} and 200 mg kg^{-1} for residential soils with and without plant uptake, respectively, 130 mg kg^{-1} for allotments and 5000 mg kg^{-1} for commercial or industrial soils. SGVs were designed to represent intervention values which, if exceeded, posed potentially unacceptable risks to site users and may require investigation or remedial action. The results of the present study indicate localised exceedance of the residential SGVs for Pb in all paint-contaminated soils, and exceedance of the commercial-industrial SGV in all but one case; in contrast, Cr concentrations in soils never exceed residential without plant uptake and commercial-industrial SGVs. For reasons that are unclear, however, the original CLEA model was withdrawn in 2006, with new SGVs subsequently issued by the Environment Agency (2009) and based on updated software that excluded both Pb and Cr. With respect to Pb, more recent evidence for neurotoxicity at lower exposure levels was cited as status for 'reconsideration', but for Cr, a rationale for withdrawal of SGVs does not appear to have been provided.

3.4. Heavy metal bioaccessibility in soils

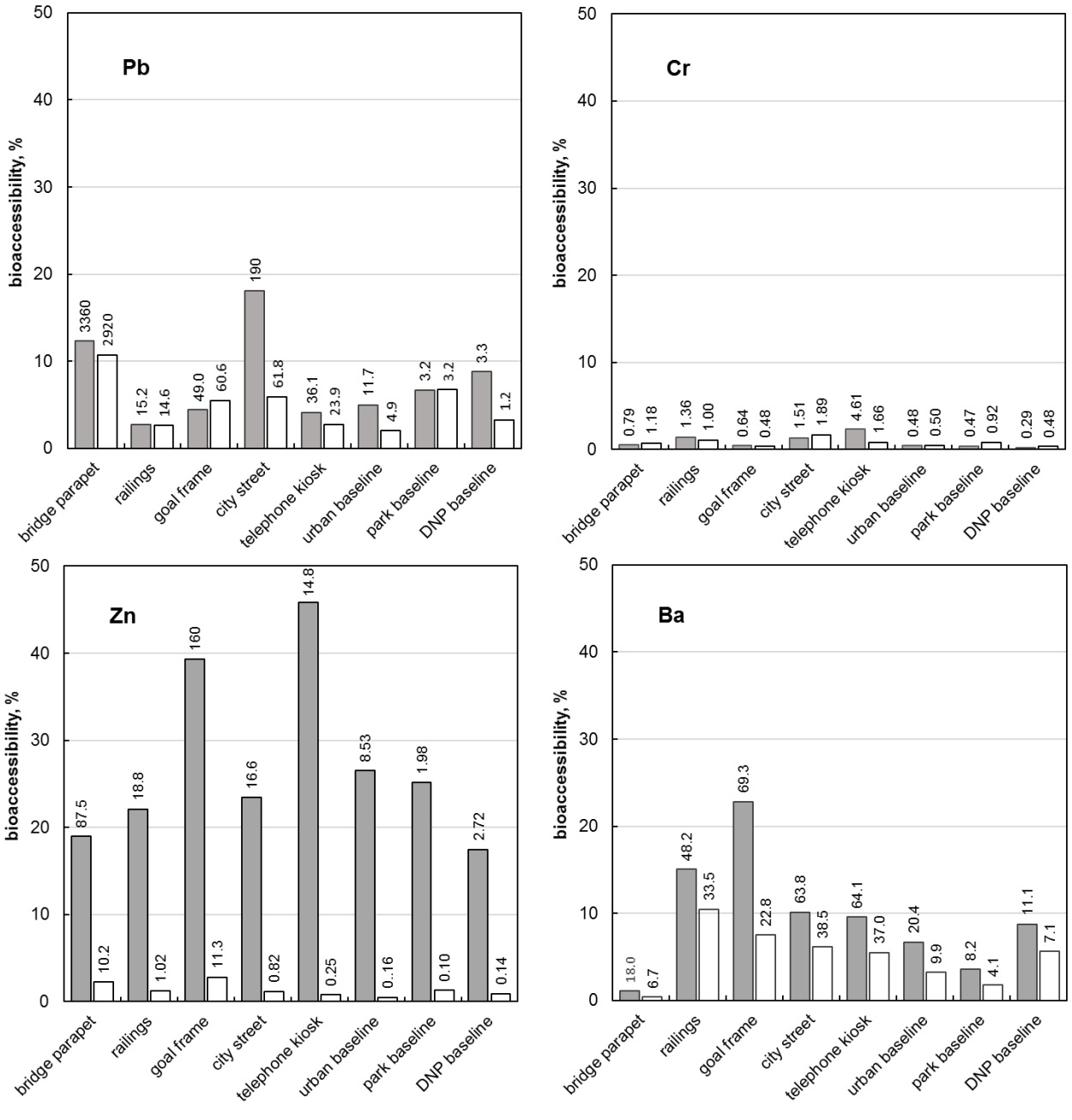
Aside from their absolute concentrations, critical to the health risks of heavy metals in contaminated soils is their bioaccessibility, or their propensity to migrate from the

ingested or inhaled material into physiological solutions. In this study, a two-stage, sequential PBET was used to evaluate the bioaccessibilities of Pb, Cr, Zn and Ba in the < 2 mm fraction of soils in the human stomach and intestine, and results, on both a concentration and percentage (relative to total metal) basis are illustrated in Figure 3.

In the stomach phase, the bioaccessibility of Pb ranges from about 3 to 18%, with concentrations varying from around 3 mg kg^{-1} in two baselines to over 3000 mg kg^{-1} (and well in excess of SGVs based on total Pb) in the bridge parapet soil. In most cases, bioaccessibility is lower in the intestine than in the stomach because the higher pH in the former favours the re-adsorption of Pb^{2+} ions to the soil particle surface and the precipitation of relatively insoluble Pb species (Turner and Ip, 2007). The percentage bioaccessibility of the metal in either phase of the PBET does not appear to be directly related to its total concentration in the matrix, nor to the geochemical characteristics of the soil. Rather, it is likely that accessibility is dependent on the nature and degree of metal-soil particle interactions, which themselves are controlled by the age and condition of the applications and the solubilities of the component leaded pigments (Walraven et al., 2015).

Chromium bioaccessibility is considerably lower than that of Pb, presumably because of the relatively poor solubility of chromate pigments, with percentages never exceeding 2.5 in either of the simulated PBET phases but that were higher in the intestine than the stomach in five cases. The latter effect may be attributed to the existence of negatively charged, polyatomic forms of Cr(VI) whose desorption from the contaminated soil matrix is predicted to be promoted in the higher pH environment of the intestine (Villalobos et al., 2001). Zinc exhibits the greatest

465 percentage accessibility in the stomach phase among the metals studied (between
466 about 15 and 45%). However, the higher pH of the simulated intestine ensures that,
467 through readsorption of Zn^{2+} ions to the soil matrix, intestinal accessibility never
468 exceeds 3% of total Zn. While Ba exhibits lower percentage stomach
469 bioaccessibilities than Zn, less readsorption of Ba^{2+} ions at higher pH results in
470 intestinal accessibilities that are generally greater (and by up to an order of
471 magnitude) than corresponding values for Zn.
472
473 Given that absorption takes place primarily in the intestinal epithelium, the heavy
474 metal concentration remaining in the simulated intestine may provide the most
475 relevant estimate of its bioavailability, or the fraction of total metal that reaches the
476 systemic circulation. In the present study, the mean percentage intestinal accessibility
477 in the five contaminated soils was in the order: Pb, Ba (~ 6) > Zn (1.6) > Cr (0.9);
478 with variations in precise accessibilities reflecting differences in the nature and age of
479 the contaminating paint, the type and characteristics of the local soil, and the presence
480 of additional, and more diffuse metal sources.



481

482 Figure 3: Percentage stomach and intestinal bioaccessibilities (shaded and white bars,

483 respectively) of Pb, Cr, Zn and Ba in the soil samples. Annotated are the

484 corresponding bioaccessible concentrations in mg kg^{-1} .

485

486 *3.5. General discussion*

487 This study has shown that legacy leaded paint is a characteristic of functional

488 structures in residential areas of south west England. While the painted areas

themselves are relatively small, the structures are commonplace throughout the UK and are generally accessible to the public and close to sensitive receptors (houses, schools, hospitals). For example, there are about 11,000 K6 telephone kiosks in service throughout the UK that are owned by British Telecom (BT) and over 28,000 railway bridges managed by Network Rail. With little requirement or incentive to maintain the décor of telephone kiosks that have seen a rapid decline in usage, or to repair the extant, metallic components of disused railway bridges, a consequence is extensive flaking or crumbling from overpainted layers that affords a direct means of contaminating local soil and road dusts with heavy metals. Contamination of surface runoff, ground water and storm waters may then occur through the dissolution of metals from soil and dust into rainwater, an effect accentuated by low pH and the presence of complexants (Davis and Burns, 1999; Wu and Kim, 2017).

From a health perspective, and based on its known chronic neurotoxicity and the concentrations and intestinal accessibilities in contaminated soils, Pb is the metal of greatest concern amongst those considered in this study. Although Pb contamination is localised, there is a direct risk of metal exposure to children in turfed play parks containing painted equipment through the inadvertent or deliberate ingestion of contaminated soil while playing (Stanek et al., 2012). More generally, the location of poorly maintained structures in residential areas poses risks of Pb exposure indoors from intruding airborne dust generated through resuspension by wind and moving traffic, and by material tracked-in on clothes and shoes and on the feet of family pets (Laidlaw et al., 2014); here, entry into the household setting is likely to be accentuated in the summer months when soil is drier and looser and properties are more ventilated, resulting in a distinct seasonal variation in exposure. Flaking paint itself also poses a

direct risk of Pb exposure to contractors maintaining, repainting, restoring or demolishing structures and affords an additional indirect means by which the metal may be introduced into the household via clothing, hair or shoes (Virji et al., 2009). We note that a recent Office of Rail Regulation (2014) report refers to six cases of employee absence through elevated blood Pb levels over a three year period, and that all personnel were working on refurbishment of railway bridges or stations involving cutting and/or surface treatment of painted surfaces.

We contacted the stakeholders or responsible authorities in respect of the types of structures considered in the present study and received responses that were generally proactive, but only localised and short-term. For example, BT either removed or repainted telephone kiosks within the city of Plymouth, while Network Rail acknowledged that there was a problem with leaded paint and suggested that the particular bridge we identified may be prioritised for repainting. Plymouth City Council decommissioned a number of playground facilities known to contain leaded paint after being alerted to findings from a more specific, earlier survey (Turner et al., 2016), but were not receptive to a broader investigation or remediation of the general problem.

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539

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